PTO 06-3430

French Patent Application
Document No. 2,181,607

METHOD AND PRODUCTS FOR NEUTRALIZING SMOKE THAT COMES FROM THE BURNING OF FUELS THAT CONTAIN SULFUR
[PROCEDE ET PRODUITS POUR LA NEUTRALISATION DES FUMEES PROVENANT DE LO COMBUSTION DES COMBUSTIBLES CONTENANT DU SOURFRE]

H. Nawrocki

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. MARCH 2006

Translated by: Schreiber Translations, Inc.

Country	:	France
Document No.	:	2,181,607
Document Type	:	French Patent Application
Language	:	French
Inventor	:	H. Nawrocki
Applicant	:	H. Nawrocki
IPC	:	C 10 I 10/00
Application Date	:	19720427
Publication Date	:	19731207
Foreign Language Title	:	Procede et produits pour la neutralisation des fumes provenant de la combustion des combustibles contenant du soufre
English Title	:	Method and products for neutralizing smoke that comes from the burning of fuels that contain sulfur

METHOD AND PRODUCTS FOR NEUTRALIZIGN SMOKE COMING FROM THE BURNING OF FURLS THAT CONTAIN SULFUR

The present invention concerns a method and products for neutralization smoke that comes from the burning of fuels that contain sulfur. These products and method in particular have the goal to protect against the corrosion of exchange surfaces that come into contact with the fumes, to prevent the formation of soot that hinders good heat transfer and to prevent environmental pollution.

It is known that the burning of solid, liquid or gaseous fuels that contain sulfur can cause corrosion of metal surfaces that come into contact with the fumes that result from this burning.

Indeed, the burning of sulfur in the form of sulfurous anhydride SO2 leads to the formation of sulfuric anhydride SO3 due to the catalytic action of ferric sulfate (Fe(SO4)3.

In addition, the presence of the vanadium contained in certain fuels aggravates the corrosion, because it acts as a catalyst. Its presence is particularly responsible for accelerating the corrosion at high temperature, in super-heaters of industrial and marine boilers.

---

[1] Numbers in the margin indicate pagination in the foreign text.

Low temperature corrosion is due to the presence of the SO3 that increases greatly the dew point of the smoke whose contact with the relatively cold surfaces causes condensation of the SO3 that leads to the formation of sulfuric acid H2SO4. This phenomenon can be produced, especially, in air and water reheaters and in steam generator fireboxes. Environmental pollution by SO3 and H2SO4 can finally be the cause of serious damage.

The present invention proposes to overcome the disadvantages mentioned above.

According to a first characteristic, the method according to the invention consists in adding to the fuel, or possibly to the combustion air, in the firebox or in the smoke of the boilers, or even in the combustion air of diesel engines, an additive based on iron.

According to another characteristic the method according to the invention is remarkable in that one adds to the liquid fuel a liquid solution that contains from 1 to 10% by weight of iron.

The product used as a neutralizing agent, for example, can be iron naphthenates that contains 6% iron by weight. /2

In order to reduce the viscosity of the composition, one will add to the aforementioned solution an adequate solvent such as, for example, a hydrocarbon with Luchaire flash point greater than 65°C.

In this case the composition of the neutralizing agent that results from this mixture could advantageously be:

- 40 to 60% and, for example, 50% of a solution such as iron naphthenates that contains from 1 to 10% iron by weight, and;
- 60 to 40$ and, for example, 50% solvent.

In order to promote the miscibility of the additive and the fuel, it is also provided that one can add to the above ingredients an appropriate wetting agent such as oxyethylenated Nonylphenol with nine molecules.

As an example, the neutralizing solution can be comprised, in this case, of:

- 40 to 55% and, for example, 45% of a solution such as iron naphthenates that contains from 1 to 10% iron by weight;
- 40 to 55% and, for example, 45% of a suitable solvent;
- 5 to 20% and, for example, 10% of a wetting agent.

Finally, one can even combine with the aforementioned ingredients a demulsifier to break up the water/fuel emulsions. This demulsifier can advantageously be comprised of an ethylene oxide on polypropylene glycols.

The neutralization solution could then have the following composition:

- 40 to 50% and, for example, 45% of a product such as iron naphthenates, which contains from 1 to 10% iron by weight;

- 40 to 50% and, for example, 45% of a suitable solvent;
- 5 to 15% and, for example, 5% of a wetting agent;
- 5% demulsifier.

The additive or smoke demulsifier according to the invention is simply added to the fuels in proportions that can vary slightly.

In a general way the studies carried out by the applicant allowed him to determine that vary small quantities of iron, on the order of 0.002 grams atomic weight of iron per liter of fuel, are sufficient to yield the desired results that will be emphasized subsequently in the present description. /3

The cost of treating liquid fuels with the iron based additive according to the invention is therefore reduced quite a bit. Indeed, the quantities of neutralizer necessary to obtain the excellent results presented subsequently are so low that their application on a large scale of the method is possible at particularly low return costs.

One advantage of the iron based additives according to the invention is their use of use. No injection device or dispensing apparatus is necessary.

The mixture of additives and fuels, prior to the use or combustion of the latter, is achieved simply by adding, for example, the additives to the tanks before storage of the fuels, the mixing being carried out separately.

It is suggested that one could use one liter of additive or neutralizer per 3 to 20 tons of fuel, with low, medium or heavy viscosity, in order to obtain the measured dose of 0.002 grams atomic weight of iron per liter of fuel.

The research of the applicant have led to economical products, a method that is practical and easy to put into operation, and with extremely satisfactory results in the battle against the annoying problems mentioned earlier and caused by the use of fuels that contain sulfur.

The following advantages are emphasized in particular:

a) Improved burning of the fuel due to the oxidizing effects of the iron;

b) Effective protection against the corrosion of all surfaces in contact with the fumes, because a very fine layer of iron is deposited on the heat exchange surfaces or on those of the smokestacks. This protection is obtained also at high temperatures, in super-heaters for example as well as at low temperatures, especially in air or water reheaters or boiler economizers. One can thereby achieve a reduction in shutdowns needed for maintenance and labor savings;

c) One can obtain friability of the deposits that possibly exist on the exchange surfaces, which allows easy removal of these deposits by ordinary boiler tube cleaning whose frequency is reduced; /4

d) Protection against the formation of burned deposits (soot) and ashes on the heat exchange surfaces and smokestacks and, consequently, an improvement of thermal yield;

e) Lowering of the dew point of the smoke;

f) Very significant reduction of the percentage of SO3, on the order of 60 to 80% based on the individual case, contained in the fumes, which is largely beneficial for the environment;

g) Considerable reduction of emissions of dust particles contained in the fumes, generally on the order of 60 to 80% based on the individual case;

h) Fuel economy that results from the improvement of the heat exchangers.

The excellent results that derive from the chemical treatment according to the method of the invention are also due to lowering of the percentage of SO3 contained in the fuel ashes.

It is known that a fuel whose ashes contain a percentage of SO3 less than 3-5%, burned without major problems of corrosion, of formation of deposits on the exchange surfaces and atmospheric pollution.

On the contrary, fuels whose analysis of the ashes reveals a percentage of SO3 greater than about 10% often give rise to the appearance of the listed annoying problems.

The method of the applicant consists therefore in incorporating in the fuels small quantities of iron in solution

in other ingredients such as solvents and surfactants, so as to allow one to restore an analysis of the ashes with low percentage of SO3.

A repetition of the analysis of fuel ashes that yield a percentage less than 5-10% of SO3 is not however always necessary, because the iron contained in the additive is present in a mono-molecular liquid form and considerably disturbs the noxious effects of the sulfur, even is the latter is present in a percentage greater than 5-15% in the analysis of the ashes.

Another advantage that results from the use of the products and method according to the invention is that they do not cause any formation of deposits on the heat exchange surfaces of the boilers and diesel engines, with respect to smoke. /5

The presence of such deposits is often determined when one uses traditional neutralizers based on calcium carbonate or dolomite, or any other powder or liquid product introduced into the combustion air, or into the smoke, or into the fuels themselves. /6

CLAIMS

1. Method for the neutralization of smoke that comes from the burning of solid, liquid or gaseous fuels that contain sulfur and, in particular, liquid fuels such as fuels that are characterized in that the additive or neutralizing agent used is a product or a solution based on iron.

2.Method for the neutralization of smoke that comes from the burning of fuels that contain sulfur and, in particular, liquid combustible materials such as fuels according to claim 1 characterized in that one adds to the said fuels a liquid solution containing from 1 to 10% iron by weight.

3. Method according to claim 2 characterized in that the said liquid solution is comprised of iron naphthenates that contains, for example, about 6% iron by weight.

4. Method according to claims 2 or 3 characterized in that the neutralizing agent added to the fuel is comprised of a mixture that includes a solution containing from 1 to 10% iron by weight and a suitable solvent, especially a hydrocarbon with flash point greater than 65°C, the mixture having, preferably, the following composition:

- 40 to 60% and, more precisely, 50% of a solution based on iron;
- 60 to 40% and, more precisely, 50% solvent.

5. Method according to claim 4 characterized in that the neutralizing agent added to the fuel is comprised of a mixture that includes: a solution containing from 1 to 10% iron by weight, a suitable solvent and a surfactant such as, especially, oxyethylenated Nonylphenol with 9 molecules, the said mixture having, preferably, the following composition:

- 40 to 55% and, more precisely, 45% of a solution based on iron;
- 40 to 55% and, more precisely, 45% of a suitable solvent;
- 5 to 20% and, more precisely, 10% of a surfactant.

6. Method according to claim 5 characterized in that the neutralizing agent incorporated in the fuel is comprised of a mixture that includes: a solution containing from 1 to 10% iron by weight, a suitable solvent, a surfactant and a demulsifier to break down the water/fuel emulsions, especially an oxide of ethylene on polypropylene glycols, the said mixture having, preferably, the following composition:

- 40 to 50% and, more precisely, 45% of a solution containing iron;
- 40 to 50% and, more precisely, 45% of a suitable solvent;
- 5 to 15% and, for example, 5% of a surfactant;
- 5% of a demulsifier.

7. Method according to any of the claims 2 to 6 characterized in that one uses about one liter of neutralizing agent for the treatment of 3 to 20 tons of fuel, so as to incorporate a quantity of iron on the order of 0.002 gram atoms per liter of fuel.

8. Product for the neutralization of smoke that comes from the burning of fuels containing sulfur and, in particular, liquid combustible materials such as fuels, characterized in that it is

comprised of a mixture that includes a liquid solution containing from 1 to 10% iron by weight such as, for example, iron naphthenates, and a suitable solvent such as, for example, a hydrocarbon with flash point greater than 65°C, the composition of this product being, preferably:

- 40 to 60% and, especially, 50% of a liquid solution containing from 1 to 10% iron by weight, and of;
- 60 to 40% and, especially, 50% of a suitable solvent.

9. Product for the neutralization of smoke coming from the burning of combustible materials that contain sulfur according to claim 8 characterized in that it is comprised of a mixture that includes also a suitable surfactant such as, for example, oxyethylenated Nonylphenol with 9 molecules, the composition of this product being, preferably:

- 40 to 55% and, especially, 45% of a liquid solution that contains from 1 to 10% iron by weight;
- 40 to 55% and, more precisely, 45% of a suitable solvent;
- 5 to 20% and, for example, 10% of a surfactant.

10. Product for the neutralization of smoke coming from the burning of combustible materials containing sulfur according to claim 9 characterized in that it is comprised of a mixture that also includes a demulsifier to break down the water/fuel emulsions such as, for example, an oxide of ethylene on the

polypropylene glycols, the composition of this product being, preferably:

- 40 to 50% and, especially, 45% of a liquid solution that contains from 1 to 10% iron by weight;
- 40 to 50% and, for example, 45% of a suitable solvent;
- 5 to 15% and, more precisely, 5% of a surfactant;
- 5% of a demulsifier.